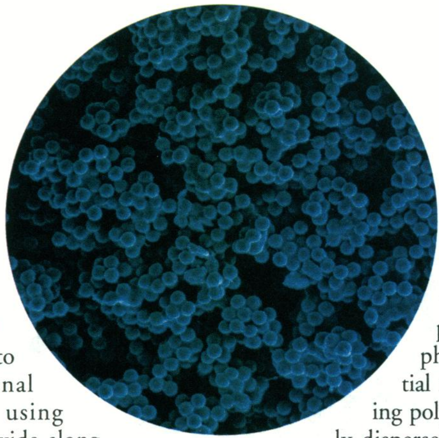
Promising Polymers



Joseph M. DeSimone

Driven to discover an environmentally responsible method for manufacturing plastics, a team of research chemists at the University of North Carolina at Chapel Hill recently devised a way to polymerize conventional lipophilic monomers using supercritical carbon dioxide along with an added stabilizer. Not only does the process eliminate many of the toxic by-products generated in conventional polymer manufacturing, it also holds bright prospects for the creation of altogether new polymeric materials, whose properties and potential applications are just beginning to be discovered.

Supercritical carbon dioxide is a highly pressurized form of the chemically benign gas that has properties of a liquid. Although the food industry has used supercritical carbon dioxide to decaffeinate coffees and teas, Joseph DeSimone, a professor of chemistry at UNC, is applying the same technology to polymer synthesis. DeSimone and his colleagues successfully employed supercritical carbon dioxide as the dispersing medium to polymerize a lipophilic monomer known as methyl methacrylate (MMA), which is used to make plexiglass. Using a free-radical initiator, as well as an additive to stabilize the dispersion of monomers into growing plastic particles, researchers created a product with uniform morphology and high molecular weight. Over time, chemical companies may be able to apply this technology to plastics production and curb the use of hazardous organic solvents, which present risks to human health.

Traditional Plastics Processing

In conventional polymer manufacturing, monomers, the initial kernels of the chemical reaction that produces polymers, are suspended in large quantities of water or chemical solvents. According to DeSimone, polymers produced on a large scale such as polystyrene, polyvinyl chloride (PVC), polyethylene co-vinylacetate, polyacrylic acid, and styrene and butadiene rubber, are created using heterogeneous dispersion polymerization. In this process, polymers form in two phases in which the initial monomer or the resulting polymer, or both, are finely dispersed in a solvent and are controlled by adding a surfactant (stabilizer) that conforms particle sizes to within a relatively narrow range. Once the polymers are formed, manufacturers remove the water or evaporate the solvents used to disperse the polymers. Companies then face the challenge of properly disposing of and remediating these harmful by-products—a daunting task as EPA regulations grow more stringent. In 1992, the U.S. plastics industry produced 567 million pounds of toxic waste, according to the EPA. In the same year, companies put about one-quarter of their total waste back into the nation's environment.

Because most organic solvents (typical ones include toluene and methylene chloride) are petroleum-based, many are flammable, volatile, and often cause narcotic effects to humans at high concentrations. Yet pharmaceutical, chemical, and polymer industries must use vast amounts of these solvents to extract, separate, and manufacture chemicals.

According to Paul Anastas, chief of the new chemicals section in the EPA's Office of Pollution Prevention and Toxics in Washington, DC, these solvents have "serious health implications." Companies that release these solvents must comply with various requirements, says Anastas: "They have to be concerned with waste treatment and control, [monitoring] water effluent and air emissions, and minimizing exposure to workers."

Human health stands to benefit from polymerization using supercritical carbon dioxide because the process avoids the use of harmful solvents that are known health hazards, contends DeSimone, whose research is funded through the Environmentally Benign Chemical Synthesis and Processing Program sponsored by the EPA and the National Science Foundation. Manufacturers have traditionally dealt with toxic by-products in two ways: remediation and control. "What we're talking about now is a new option for dealing with waste-avoidance," DeSimone says.

Therein lies this technology's single greatest advantage, says Anastas: "Natural carbon dioxide is absolutely innocuous. The gas is harmful only if it is produced through combustion. "If you're just converting existing carbon dioxide, there is no harm," Anastas explains. After the polymers form, the carbon dioxide is simply depressurized, returning it to a gaseous state, and is then vented off. Anastas quickly offers further reassurances: "The use of carbon dioxide is not going to contribute to the greenhouse effect; only the creation of carbon dioxide [is going to do that]."

Manipulating the Magic Medium

DeSimone conducted his research with the help of five colleagues—Elise Maury, James McClain, Timothy Romack, Yusaf Menceloglu, and James Combes. Their efforts stemmed from work DeSimone published in 1992, when he was successful in synthesizing high molecular weight fluoropolymers in supercritical carbon dioxide using homogeneous free-radical polymerization methods. However, DeSimone explains, fluoropolymers, along with silicones, are exceptions to the rule: Most polymers with high molecular weights are not significantly soluble in supercritical carbon dioxide.

To stabilize the polymerization of lipophilic monomers such as MMA, DeSimone and his research team would have to find a molecule that is interfacially active with the carbon dioxide. It would feature both a carbon dioxide-philic segment that would dissolve easily in carbon dioxide, and a carbon dioxide-phobic segment that would create a lipophilic backbone that could adsorb onto an acrylic suspended particle and serve as an anchor for the carbon dioxide-philic steric stabilizing moities. The team also used two free-radical polymerization initiators, known as AIBN and F-AIBN, which are highly soluble in carbon dioxide and can selectively partition into a continuous supercritical carbon dioxide phase.

Next, the team set to work on polymerizing MMA with and without an added stabilizer. They set up the homogeneous polymerizations in a 10-milliter, high-pressure reaction view-cell equipped with a magnetic stir bar and sapphire windows, which enabled them to watch the phase behavior during the polymerization. After purging the cell with argon gas for 10 minutes, the team injected the MMA monomer and filled the cell with carbon dioxide. They then heated the cell and raised the pressure inside by adding more carbon dioxide.

After four hours, the reactor was cooled and the carbon dioxide vented. DeSimone and his colleagues found that, without the addition of a stabilizer for both initiators, the polymethyl methacrylate that formed in the polymerization process accumulated in a thick, irregular film on the walls and windows inside the view cell. Scanning electron microscopy subsequently revealed these precipitated, unstabilized particles possessed a nondescript morphology as well.

Dispersion polymerizations performed with an added stabilizer, however, produced dramatically different results. This time, the cell became increasingly clouded with polymers forming a kinetically stable suspended dispersion. In this case, the stabilizer, poly(FOA), proved to be interfacially active in the supercritical carbon dioxide, creating a stable colloid. This result, DeSimone and colleagues reported, indicated a steric stabilization mechanism comparable to that obtained in conventional heterogeneous polymerizations using nonionic surfactants. And the use of either poly(FOA) as a stabilizer produced polymers with considerably higher yield and molecular weights. The resulting product, a free-flowing powder made of particles ranging in size from 0.9 to 2.7 microns, was easily isolated as the carbon dioxide was vented.

In subsequent tests, DeSimone's research team varied the combinations of initiators and stabilizers so they could compare the results. They discovered that the size and uniformity of particles formed during the polymerizations depended on the stabilizer's molecular weight, as well as the amount added to the reaction. They also concluded that the compressibility of the supercritical phase allows variations in polymer morphology, perhaps leading to "new core shell structures, interpenetrating polymer networks, or new composite materials," results that cannot be obtained using conventional solvents.

Assessing the Industry Impact

Supercritical fluid technology is not brand new. The first supercritical fluid was created more than 100 years ago. Low-density polyethylene was first manufactured 60 years ago using supercritical fluids. The food industry taps into the technology primarily to extract unwanted elements: caffeine from coffee and tea, impurities from spices, and oils from the hops used to make beer. Besides extraction, supercritical fluids can be used as release agents when placing an additive in a material, or for processing existing materials.

Union Carbide, for example, uses supercritical carbon dioxide as a thinner for industrial spray-painting, which has allowed the company to reduce up to 80% of its hazardous emissions from that process. DeSimone's research adds a new dimension, however, effecting a chemical reaction in a supercritical fluid.

F. Peter Boettcher, manager of external technology at Dupont's Central Research and Development, cautions that this technology is still in the very early stages. "It is certainly a very interesting approach to trying to solve some of our environmental problems," Boettcher concedes. "However, it is difficult to extrapolate from this to large-scale industrial applications. Fundamentally, new technologies take anywhere from 5 to 10 years before they become a commercial reality." Nevertheless, DuPont, Hoechst Celanese, BFGoodrich, AirProducts and Chemicals, and Eastman Chemical have invested more than idle interest in DeSimone and his colleagues' efforts. Together they have formed a consortium to help finance further research in this area.

"The fact that they are interested means that this research is very important to them," says Margaret Cavanaugh, program director in the chemistry division of the National Science Foundation, which has partially funded DeSimone's research. While Cavanaugh doesn't expect chemical companies to completely overhaul their manufacturing methods, she does see DeSimone's technology replacing certain parts of the process. George A. Serad, a technical manager in strategic business development with Hoechst Celanese's fibers and film group, agrees: "It could provide a step change along the path to making a polymer," he says.

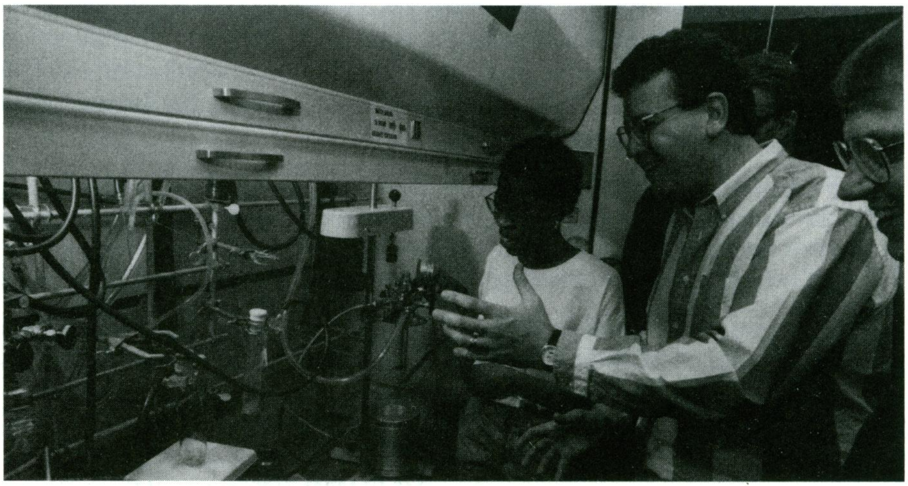
The New Materials Frontier

DeSimone's research not only gives manufacturers a cleaner method of making polymers, it also points the way to new, superior plastics with as-yet unfathomed applications. Jacquelynn Savoca, a polymer scientist at the BFGoodrich Research and Development Center in Brecksville, Ohio, is involved in technology acquisition and "always looking for new, environmentally responsible ways to make polymers." This technology is a "two-fer," she says, because it "gives results you can't get with the standard method [of producing polymers] and you get a new type of polymer in a way that is environmentally benign. Certain reactions occur more rapidly in supercritical fluids than in standard solvents. Certain catalysts respond more efficiently," she says.

Serad refers to supercritical carbon dioxide as a "tuneable" solvent. By varying the amount of pressure present in the supercritical fluid, or changing the temperature, a chemist can tinker with the fluid's molecular density, opening avenues to new substances. The density of liquid solvents used in conventional polymer synthesis is static, giving chemists little leeway in setting up new chemical reactions.

"Supercritical carbon dioxide opens the door to new materials with new properties," says DeSimone. Using this form of the gas, scientists can exercise more control over the molecular weight and composition of polymers than previous techniques have allowed. Research has shown that plastics made with carbon dioxide are not only equal to other plastics in quality, but actually superior.

"We want to see if supercritical fluid



UNC Dept. Of Chemistry

Polymers in progress. Joseph M. DeSimone explains his new technique for making environmentally friendly polymers to a group of graduate students.

technology is applicable to the manufacture of polyester," Serad said of the interest Hoechst Celanese has shown toward DeSimone's research. Specifically, the company envisions using supercritical carbon dioxide to dissolve polymers, synthesize them, or depolymerize a product back to its original raw materials. According to Serad, supercritical carbon dioxide also shows considerable promise in that it supports the synthesis of finer, more uniformly sized particles. Such an advance may be welcomed by the pharmaceutical industry, where the technology could be used to "enhance drug delivery," explains DeSimone. Companies could use this method to manufacture drugs that may diffuse more efficiently into the human body. Elsewhere in industry, in cosmetics manufacturing, for example, supercritical carbon dioxide could be used as a carrier medium for dyes.

Weighing the Costs

New applications aside, a cleaner method for manufacturing polymers could translate into worthwhile cost savings for chemical companies. By eliminating the use of volatile organic compounds and conducting environmentally benign polymer synthesis instead, these companies could also forgo a portion of the amount they spend on regulatory compliance. They could trim some of their costly efforts to dispose of and reuse these compounds, including air scrubbing and material recovery systems.

According to the EPA, U.S. industry spent $115 billion on waste treatment and control in 1992. And with increasing scrutiny of environmental hazards from both the public and government agencies, these costs are likely to keep increasing. Polymerization in supercritical carbon dioxide could potentially offer other fiscal benefits. For one thing, carbon dioxide itself is relatively cheap—about four cents per pound, according to DeSimone—and much less expensive than organic solvents. It also requires less energy to process than organic solvents.

"It is very expensive and difficult to remove trace contaminants from water," says DeSimone. With his new method, however, plastics makers "can decompress the carbon dioxide and [easily] remove the trace contaminant," he explains. Recycling affords yet another advantage, he says: 90% of the spent carbon dioxide can be recovered cost-effectively.

However, the expense of new equipment capable of handling high-temperature, high-pressure reactions is a drawback that will force companies to carefully evaluate which processes and products could best absorb that economic impact. Companies will have to analyze total costs, including processing, clean-up, and environmental conditioning of waste products, says Serad. "As to whether it will be economically feasible, you have to look at it case by case," he says. The more expensive the product (certain pharmaceuticals, for example), the more likely a manufacturer may be able to afford the technology. "I think chemical companies have a lot of good will toward the environment," says the NSF's Cavanaugh. "But [the technology] will have to prove economically feasible. They still want to be competitive in the marketplace."

While companies ponder the pros and cons of polymer synthesis using supercritical carbon dioxide, DeSimone and his colleagues are testing approximately 30 different surfactants that are tailored to different polymers. Together with his graduate students in the chemical engineering department of North Carolina State University, DeSimone will explore and refine engineering techniques that may further this new technology as a viable polymerization process with measurable environmental benefits and perhaps speed its application in the marketplace.

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Suggested Reading

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